

Reactions of Peroxy Radical Operators with CH₃O₂

Reaction RRME

k(300)	A	Ea	Notes
2.00e-13	2.00e-13	---	39,40
RO ₂ -R. + C-O ₂ . = HO ₂ . + #.75 HCHO + #.25 MEOH			

Notes

39	Based on rate constant for methyl peroxy + ethyl peroxy rate given by Atkinson (1997a). This is near the middle of the range of rate constants given for other methyl peroxy + higher alkyl peroxy radical reactions given by Atkinson (1997a) or Atkinson et al (1997a).
40	Approximately half of the peroxy + peroxy reaction is assumed to form two O ₂ + alkoxy radicals. The HO ₂ represents the radicals regenerated in the fraction of this peroxy radical which reacts in this way.

The rate constant is consistent with the evaluation. The 0.25 yield of MEOH (CH₃OH) is consistent with current knowledge of the rate of the H-atom transfer reaction; this assumption should be added to the footnote.

Reaction R2ME

k(300)	A	Ea	Notes
Same as Reaction RRME		42,43	R2O ₂ . + C-O ₂ . = C-O ₂ .

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO ₂ -R.).
43	The R2O ₂ . operator represents the effects of peroxy radical reactions causing extra NO to NO ₂ conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

This treatment of the R2O₂. + C-O₂. reaction is consistent with the other R2O₂. reactions. The rate constant is discussed under Reaction RRME.

Reaction RNME

k(300)	A	Ea	Notes
Same as Reaction RRME		42,44, 46	RO2-N. + C-O2. = HO2. + #.25 MEOH + #.5 {MEK + PROD2} + #.75 HCHO + XC

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
44	The RO2-N. operator represents the effects of peroxy radicals which react with NO to form higher organic nitrates (represented by RNO3), and also the effects of peroxy radical reactions on other species. It has five carbons.
46	Approximately half of the peroxy + peroxy reaction for radicals represented by RO2-N. is assumed to form two O2 + alkoxy radicals. The MEK + HO2. represents the products and radicals formed from the alkoxy radical from this species. The other half is assumed to involve disproportionation, forming O2 + and an alcohol and carbonyl compound. These are represented by PROD2.

The rate constant is discussed under Reaction RRME. The 0.25 yield of MEOH (CH3OH) is consistent with current knowledge of the rate of the H-atom transfer reaction; this assumption should be added to the footnote.

Reactions of Peroxy Radical Operator Cross Reactions

Reaction RRR2

k(300)	A	Ea	Notes
3.00E-14	3.00E-14	---	41,40 RO2-R. + RO2-R. = HO2.

Notes

41	The rate constants for peroxy + peroxy radical reactions can vary by orders of magnitude depending on the type of radical (e.g., Atkinson, 1997), so the value used here must be approximate. Value used is based roughly on range of rate constants for secondary peroxy radicals as given by Atkinson (1997a).
40	Approximately half of the peroxy + peroxy reaction is assumed to form two O2 + alkoxy radicals. The HO2 represents the radicals regenerated in the fraction of this peroxy radical which reacts in this way.

The rate constant may be valid but the rationale seems weak. Atkinson recommends a rate constant of $5\text{E-}15 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for general secondary RO2 + secondary RO2 while for the rate parameter for the reaction of general primary is recommended to be $2.5\text{E-}13 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The geometric average of the primary and secondary rate parameters is $3.5\text{E-}14$ and that may be a bit better to use.

Reaction R2RR

k(300)	A	Ea	Notes
Same as Reaction RRR2		42,43,40	R2O2. + RO2-R. = RO2-R.

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.
40	Approximately half of the peroxy + peroxy reaction is assumed to form two O2 + alkoxy radicals. The HO2 represents the radicals regenerated in the fraction of this peroxy radical which reacts in this way.

The rate parameter is discussed under Reaction RRR2. The treatment of this cross reaction is reasonable because its purpose is to consume R2O2. by RO2-R.

Reaction R2R3

k(300)	A	Ea	Notes
Same as Reaction RRR2		42,43	R2O2. + R2O2. =

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

The rate parameter is discussed under Reaction RRR2. The treatment of this cross reaction is reasonable because its purpose is to consume R2O2. by R2O2.

Reaction RNRR

k(300)	A	Ea	Notes
Same as Reaction RRR2		42,44,46	RO2-N. + RO2-R. = HO2. + #.5 {MEK + PROD2} + O2 + XC

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
44	The RO2-N. operator represents the effects of peroxy radicals which react with NO to form higher organic nitrates (represented by RNO3), and also the effects of peroxy radical reactions on other species. It has five carbons.
46	Approximately half of the peroxy + peroxy reaction for radicals represented by RO2-N. is assumed to form two O2 + alkoxy radicals. The MEK + HO2. represents the products and radicals formed from the alkoxy radical from this species. The other half is assumed to involve disproportionation, forming O2 + and an alcohol and carbonyl compound. These are represented by PROD2.

The rate parameter is discussed under Reaction RRR2. The treatment of this cross reaction is consistent with the treatment in previous reactions of RO2-N. and RO2-R.

Reaction RNR2

k(300)	A	Ea	Notes
Same as Reaction RRR2		42,43	RO2-N. + R2O2. = RO2-N.

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

The rate parameter is discussed under Reaction RRR2. The treatment of this cross reaction is consistent with the treatment in previous reactions of RO2-N. and R2O2.

Reaction RNRN

k(300)	A	Ea	Notes
Same as Reaction RRR2		42,44, 46	RO2-N. + RO2-N. = MEK + HO2. + PROD2 + O2 + #2 XC

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
44	The RO2-N. operator represents the effects of peroxy radicals which react with NO to form higher organic nitrates (represented by RNO3), and also the effects of peroxy radical reactions on other species. It has five carbons.
46	Approximately half of the peroxy + peroxy reaction for radicals represented by RO2-N. is assumed to form two O2 + alkoxy radicals. The MEK + HO2. represents the products and radicals formed from the alkoxy radical from this species. The other half is assumed to involve disproportionation, forming O2 + and an alcohol and carbonyl compound. These are represented by PROD2.

The rate parameter is discussed under Reaction RRR2. The treatment of this cross reaction is consistent with the treatment in previous reactions of RO2-N.

Reactions of Acyl Peroxy Radicals, PAN, and PAN Analogues

Reaction APN2

K(300)	Falloff, F	Notes
1.04E-11	0.30	48
	A	B
k₀	2.70E-28	-7.1
k	1.20E-11	-0.9

CCO-O2. + NO2 = PAN

Notes

48	Falloff expression recommended by IUPAC (Atkinson et al, 1997a, 1999), based on data of Bridier et al (1991).
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The reactants, products and rate parameters for Reaction APN2 are consistent with current knowledge. To avoid confusion the rate expression should be given in a separate table.

Reaction DPAN

k(300)	Falloff, F	Ea	Notes
7.04E-04	0.30		49
	A		B

PAN = CCO-O2. + NO2

k_o	4.90E-03	24.05	0
k	4.00E+16	27.03	0

Notes

49	Falloff expression recommended by IUPAC (Atkinson et al, 1992), based on data of Bridier et al (1991). Note: NASA (1997) also recommends using Bridier et al (1991) data, but gives a revised expression which gives a different k at 298K. Based on new data on PAN decomposition which give a factor of ~2 lower rate 298K rate constants, IUPAC (1997a, 1999) recommends a high pressure rate constant expression of $5.4 \times 10^{16} \exp(-13830/T)$, derived by averaging the data. We are staying with the earlier IUPAC Recommendations based on the data of Bridier et al (1991) because it gives good agreement with the data of Tuazon et al (1991) and is consistent with the NASA (1997) recommended equilibrium constant.
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The reactants and products for Reaction DPAN are consistent with current knowledge. The choice of rate constant is reasonable but more research and evaluation is required to improve this highly important rate constant.

Reaction BPN2

k(300)	A	Ea	Notes	
1.37E-11	1.37E-11	---	60	BZCO-O2. + NO2 = PBZN

Notes

60	Rate constant based on k(NO2)/k(NO) ratio measured by Kirchner et al (1992) and the k(NO) used for general higher acyl peroxy radical species.
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The rate parameter for Reaction BPN2 is consistent with the product of the k(NO2)/k(NO) ratio (measured by Kirchner as 0.62) and the rate parameter for the reaction of higher acyl radicals with NO ($2.18 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

Reaction BPAN

k(300)	A	Ea	Notes	
4.27E-04	7.90E+16	27.82	61	PBZN = BZCO-O2. + NO2

Notes

61	Rate constant expression based on the data of Kirchner et al (1992).
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The reactants, products and rate parameter for Reaction BPAN are consistent with current knowledge.

Reaction PPN2

k(300)	A	B	Notes	
1.20E-11	1.20E-11	-0.9	56,57	RCO-O2. + NO2 = PAN2

Notes

56	The rate parameters are assumed to be approximately the same as those for the reaction of $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ at the high pressure limit. NASA (1997) and IUPAC (Atkinson et al, 1997a, 1999) give no recommendations for this rate constant for higher acyl peroxy radicals.
57	The products of the reactions of $\text{RCO-O}_2\cdot$ are based on R=ethyl . Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

The reactants, products and rate parameters are reasonable for Reaction BPN2. The rate parameter is in agreement with the results of Seefeld (1997). If the rate constant is taken to be the same as $\text{CH}_3\text{CH}_2\text{CO}_3 + \text{NO}_2$. Seefeld (1997) the measured $k(\text{NO}_2)/k(\text{NO}) = 0.43 \pm 0.07$ over the temperature range of 249-302K. This leads to a rate constant of $1.2\text{E-}11 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ if the rate parameter for the reaction of $\text{CH}_3\text{CH}_2\text{CO}_3$ radicals with NO is assumed to be $2.8\text{E-}11 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in agreement with the value chosen by Carter.

Reaction MPN2

k(300)	A	Ea	B	Notes
Same as PPN2				$\text{MA-RCO}_3\cdot + \text{NO}_2 = \text{MA-PAN}$

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue
64	$\text{MA-RCO}_3\cdot$ And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to $\text{CO}_2 + \text{CH}_2=\text{CH}(\cdot)\text{CH}_3$, while the latter reacts with O_2 to form $\text{HCHO} + \text{CH}_3\text{CO}\cdot$, as discussed by Carter and Atkinson (1996). The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

This treatment of the acyl peroxy radical and PAN analogue formed from any acrolein compound are reasonable for Reaction MPN2.

Reaction PAN2

k(300)	A	Ea	Notes
5.87E-04	2.00E+15	25.44	57,58

PAN2 = RCO-O2. + NO2

Notes

57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.
58	Rate parameters based on data for PPN. The activation energy is recommended by Atkinson (1994) for thermal decomposition of higher PAN analogues. The A factor is adjusted to yield the average k(298) for PPN as measured by Schurath and Wipprecht (1980) and Mineshos and Glavas (1991). The A factor recommended by Atkinson (1994) not used because it gives k(298) outside the range of both those measurements.

The IUPAC Supplement IV (1999) reports a rate constant of 4.4E-4 (298K) and an expression $k = 2E15 * \exp(-12800/T)$ for PPN. Should that value be used for Reaction PAN2?

Reaction MPPN

k(300)	A	Ea	Notes
4.79E-04	1.60E+16	26.8	65

MA-PAN = MA-RCO3. + NO2

Notes

65	Rate parameters from Roberts and Bertman (1992), as used by Carter and Atkinson (1996).
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The rate parameter for Reaction MPPN appears to be consistent with the available laboratory studies.

APNO Reaction and Analogs

Reaction APNO

k(300)	A	Ea	Notes
2.18E-11	2.18E-11	---	50

$$\text{CCO-O2.} + \text{NO} = \text{C-O2.} + \text{CO2} + \text{NO2}$$

Notes

50	Rate constant based on the IUPAC (Atkinson et al, 1997a) recommendation is to use $k(\text{NO})/K(\text{NO2})=2.1$ for atmospheric conditions (298K and 1 atm.), with $k(\text{NO})$ approximately independent of temperature. This is almost the same as the IUPAC(Atkinson et al, 1997a, 1999) recommended value of 2.0×10^{-11} and the NASA (1997) value of 1.8×10^{-11} .
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Although the temperature dependence of this reaction is not great, the temperature dependence as given in IUPAC (Atkinson et al, 1999) evaluation should be included as $k = 7.8\text{E-}12 \cdot \text{EXP}(300/T)$. The reactants and products are consistent with present knowledge.

Reaction PPNO

k(300)	A	Ea	Notes
Same as Reaction APNO			59,57

$$\text{RCO-O2.} + \text{NO} = \text{NO2} + \text{CCHO} + \text{RO2-R.} + \text{CO2}$$

Notes

59	Assumed to have same rate constant as corresponding reaction of CH3C(O)OO .
57	The products of the reactions of RCO-O2. are based on R=ethyl . Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

See note for Reaction APNO for comments on rate parameter. The reactants and products are consistent with the assumption that RCO-O2 is CH3CH2CO3 and that there is sufficient NO to react with all CH3CH2O2 produced to convert it to CH3CHO .

Reaction BPNO

k(300)	A	Ea	Notes
Same as Reaction APNO		62,63	BZCO-O2. + NO = NO2 + CO2 + BZ-O. + R2O2.

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See note for Reaction APNO for comments on rate parameter. The reactants and products are consistent with the stated assumptions.

Reaction MPNO

k(300)	A	Ea	Notes
Same as Reaction APNO		62,64	MA-RCO3. + NO = NO2 + CO2 + HCHO + CCO-O2.

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See note for Reaction APNO for comments on rate parameter. The reactants and products are consistent with present knowledge.

APH2 Reaction and Analogs**Reaction APH2**

k(300)	A	Ea	Notes
1.38E-11	4.30E-13	-2.07	51 CCO-O2. + HO2. = #.75 {CCO-OOH + O2} + #.25 {CCO-OH + O3}

Notes

51	Branching ratio and rate constant expression recommended by IUPAC (Atkinson et al, 1997a, 1999).
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The branching ratio and the rate parameter are consistent with Atkinson et al. (1999).

Reaction PPH2

k(300)	A	Ea	Notes
Same as Reaction APH2		59,57	$\text{RCO-O2.} + \text{HO2.} = \text{RCO-OOH} + \text{O2}$

Notes

59	Assumed to have same rate constant as corresponding reaction of $\text{CH}_3\text{C(O)OO.}$
57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

See note for Reaction APH2 for comments on rate parameter. The treatment of this reaction is consistent with present knowledge. Note 57 is not exactly correct because while 25% of the acetyl peroxy radicals react with HO_2 to produce O_3 while, in contrast, 100% of the peroxy propionyl and higher peroxy acyl radicals are assumed to react with HO_2 to produce higher peroxy organic acids.

Reaction BPH2

k(300)	A	Ea	Notes
Same as Reaction APH2		62,63	BZCO-O2. + HO2. = RCO-OOH + O2 + #4 XC

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See note for Reaction APH2 for comments on rate parameter. The treatment of this reaction is consistent with present knowledge. On Note 63 the comments given for Note 57 under Reaction PPH2 apply here too.

Reaction MPH2

k(300)	A	Ea	Notes
Same as Reaction APH2		62,64	MA-RCO3. + HO2. = RCO-OOH + O2 + XC

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See note for Reaction APH2 for comments on rate parameter. The treatment of this reaction is consistent with present knowledge. On Note 64 the comments given for Note 57 under Reaction PPH2 apply here too.

APN3 Reaction and Analogs**Reaction APN3**

k(300)	A	Ea	Notes
4.00E-12	4.00E-12	---	52 CCO-O2. + NO3 = C-O2. + CO2 + NO2 + O2

Notes

52	Rate constant from Canosa-Mass et al (1996).
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The reactants, products and rate parameter are consistent with present knowledge.

Reaction PPN3

k(300)	A	Ea	Notes
Same as Reaction APN3		59,57	$\text{RCO-O}_2\cdot + \text{NO}_3 = \text{NO}_2 + \text{CCHO} + \text{RO}_2\text{-R}\cdot$ $+ \text{CO}_2 + \text{O}_2$

Notes

59	Assumed to have same rate constant as corresponding reaction of $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$.
57	The products of the reactions of $\text{RCO-O}_2\cdot$ are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

The rate parameter is consistent with Reaction APN3. The reactants and products are consistent with the assumption that RCO-O_2 is $\text{CH}_3\text{CH}_2\text{CO}_3$ and that there is sufficient NO to react with all $\text{CH}_3\text{CH}_2\text{O}_2$ produced to convert it to CH_3CHO .

Reaction BPN3

k(300)	A	Ea	Notes
Same as Reaction APN3		62,63	BZCO-O2. + NO3 = NO2 + CO2 + BZ-O. + R2O2. + O2

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

The rate parameter is consistent with Reaction APN3. The reactants and products are consistent with present knowledge.

Reaction MPN3

k(300)	A	Ea	Notes
Same as Reaction APN3		62,64	MA-RCO3. + NO3 = NO2 + CO2 + HCHO + CCO-O2. + O2

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

The rate parameter is consistent with Reaction APN3. The reactants and products are consistent with present knowledge.

APME Reaction and Analogs**Reaction APME**

k(300)	A	Ea	Notes
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9.53E-12	1.80E-12	-0.99	53	CCO-O2. + C-O2. = CCO-OH + HCHO + O2
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Notes

53	Rate constant expression recommended by IUPAC (Atkinson et al, 1999) evaluation. As discussed there, the data are inconclusive as to the importance of the competing reaction forming CH3O + CH3CO2 + O2, but the study which indicate that it occurs, which was used in the previous IUPAC (Atkinson et al, 1997a) evaluation, indicates that it occurs less than ~15% under atmospheric conditions. Therefore, the reaction is assumed to involve disproportionation 100% of the time.
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The rate parameter is consistent with the IUPAC (Atkinson et al, 1999) evaluation. Although this choice is reasonable it must be noted that at 50 F the yield of CH3OOH may be near 25% if Horie and Moortgat (1992) as quoted in Atkinson et al. (1999) are correct. The uncertainty in the branching ratio represents a major uncertainty in this reaction.

Reaction PPME

k(300)	A	Ea	Notes
Same Reaction as AMPE		59,57	RCO-O2. + C-O2. = RCO-OH + HCHO + O2

Notes

59	Assumed to have same rate constant as corresponding reaction of CH3C(O)OO.
57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

See comments for Reaction APME. The reaction is consistent with the stated assumptions.

Reaction BPME

k(300)	A	Ea	Notes
Same Reaction as AMPE		62,63	BZCO-O2. + C-O2. = RCO-OH + HCHO + O2 + #4 XC

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See comments for Reaction APME. The reaction is consistent with the stated assumptions.

Reaction MPME

k(300)	A	Ea	Notes
Same Reaction as AMPE		62,64	MA-RCO3. + C-O2. = RCO-OH + HCHO + XC + O2

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO ₂ + CH ₂ =CH(.)CH ₃ , while the latter reacts with O ₂ to form HCHO + CH ₃ CO., as discussed by Carter and Atkinson (1996). The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See comments for Reaction APME. The reaction is consistent with the stated assumptions.

APRR Reaction and Analogs

Reaction APRR

k(300)	A	Ea	Notes
1.00E-11	1.00E-11	---	54,55 CCO-O2. + RO2-R. = CCO-OH

Notes

54	Rate constant based on values for rate constants for acetyl peroxy + methyl peroxy and CH ₃ C(O)CH ₂ OO. given by Atkinson et al (1997a).
55	This reaction is assumed to proceed primarily by disproportionation to form the organic acid and a carbonyl compound, based on data for the acetyl peroxy + methyl peroxy reaction.

The rate parameter is much closer to the IUPAC value for acetyl peroxy + methyl peroxy radical than for methyl peroxy + CH₃C(O)CH₂OO. The basis for the averaging should be given in Note 54. Given that these reactions involve operator radicals it is probably best to assume that the reactions proceed by disproportionation for simplicity. However, it is

not clear that this choice is supported by the data for the acetyl peroxy + methyl peroxy reaction, see comments about Reaction APME.

Reaction APR2

k(300)	A	Ea	Notes
Same as Reaction APRR		42,43	CCO-O2. + R2O2. = CCO-O2.

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

See comment for Reaction APRR.

Reaction APRN

k(300)	A	Ea	Notes
Same as Reaction APRR		42,55, 46	CCO-O2. + RO2-N. = CCO-OH + PROD2

Notes

42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
55	This reaction is assumed to proceed primarily by disproportionation to form the organic acid and a carbonyl compound, based on data for the acetyl peroxy + methyl peroxy reaction.
46	Approximately half of the peroxy + peroxy reaction for radicals represented by RO2-N. is assumed to form two O2 + alkoxy radicals. The MEK + HO2. represents the products and radicals formed from the alkoxy radical from this species. The other half is assumed to involve disproportionation, forming O2 + and an alcohol and carbonyl compound. These are represented by PROD2.

See comment for Reaction APRR. The treatment of the RO2-N. radical appears to be reasonable.

Reaction BPRR

k(300)	A	Ea	Notes
Same as Reaction APRR		62,63	BZCO-O2. + RO2-R. = RCO-OH + O2 + #4 XC

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
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63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO ₂ conversion, so it can be represented by BZ-O. + R ₂ O ₂ . The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.
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See comment for Reaction APRR.

Reaction BPR2

k(300)	A	Ea	Notes
Same as Reaction APRR		43,62	BZCO-O ₂ . + R ₂ O ₂ . = BZCO-O ₂ .

Notes

43	The R ₂ O ₂ . operator represents the effects of peroxy radical reactions causing extra NO to NO ₂ conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.
62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.

See comment for Reaction APRR.

Reaction BPRN

k(300)	A	Ea	Notes
Same as Reaction APRR		46,62, 63	BZCO-O ₂ . + RO ₂ -N. = RCO-OH + PROD2 + O ₂ + #4 XC

Notes

46	Approximately half of the peroxy + peroxy reaction for radicals represented by RO ₂ -N. is assumed to form two O ₂ + alkoxy radicals. The MEK + HO ₂ . represents the products and radicals formed from the alkoxy radical from this species. The other half is assumed to involve disproportionation, forming O ₂ + and an alcohol and carbonyl compound. These are represented by PROD2.
62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO ₂ conversion, so it can be represented by BZ-O. + R ₂ O ₂ . The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See comment for Reaction APRR. The treatment of the RO₂-N. radical appears to be reasonable and consistent with Reaction APRN.

Reaction PPRR

k(300)	A	Ea	Notes
Same as Reaction APRR		59,57	RCO-O ₂ . + RO ₂ -R. = RCO-OH + O ₂

Notes

59	Assumed to have same rate constant as corresponding reaction of CH ₃ C(O)OO.
57	The products of the reactions of RCO-O ₂ . are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

See comment for Reaction APRR.

Reaction PPR2

k(300)	A	Ea	Notes
Same as Reaction APRR		59,43	RCO-O ₂ . + R ₂ O ₂ . = RCO-O ₂ .

Notes

59	Assumed to have same rate constant as corresponding reaction of CH ₃ C(O)OO.
43	The R ₂ O ₂ . operator represents the effects of peroxy radical reactions causing extra NO to NO ₂ conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.

See comment for Reaction APRR.

Reaction PPRN

k(300)	A	Ea	Notes
Same as Reaction APRR		59,46,57	$\text{RCO-O2.} + \text{RO2-N.} = \text{RCO-OH} + \text{PROD2} + \text{O2}$

Notes

59	Assumed to have same rate constant as corresponding reaction of $\text{CH}_3\text{C(O)OO.}$
46	Approximately half of the peroxy + peroxy reaction for radicals represented by RO2-N. is assumed to form two O2 + alkoxy radicals. The $\text{MEK} + \text{HO2.}$ represents the products and radicals formed from the alkoxy radical from this species. The other half is assumed to involve disproportionation, forming O2 + and an alcohol and carbonyl compound. These are represented by PROD2.
57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

See comment for Reaction APRR.

Reaction MPRR

k(300)	A	Ea	Notes
Same as Reaction APRR		62,64	$\text{MA-RCO3.} + \text{RO2-R.} = \text{RCO-OH} + \text{XC}$

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. and MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to $\text{CO2} + \text{CH}_2=\text{CH(.)CH}_3$, while the latter reacts with O2 to form $\text{HCHO} + \text{CH}_3\text{CO.}$, as discussed by Carter and Atkinson (1996). The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See comment for Reaction APRR.

Reaction MPR2

k(300)	A	Ea	Notes
Same as Reaction APRR		43,62	$\text{MA-RCO3.} + \text{R2O2.} = \text{MA-RCO3.}$

Notes

43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no
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	effect other than to consume this operator.
62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.

See comment for Reaction APRR.

Reaction MPRN

k(300)	A	Ea	Notes
Same as Reaction APRR		62,64	MA-RCO3. + RO2-N. = #2 RCO-OH + O2 + #4 XC

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. and MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

See comment for Reaction APRR.

Reaction APAP and Analogs

Reaction APAP

k(300)	A	Ea	Notes
1.54E-11	2.90E-12	-0.99	31

$$\text{CCO-O2.} + \text{CCO-O2.} = \#2 \{ \text{C-O2.} + \text{CO2} \} + \text{O2}$$

Notes

31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).
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Reactants, products and rate parameter are consistent with present knowledge.

Reaction PPAP

k(300)	A	Ea	Notes
Same as Reaction APAP			59,57

$$\text{RCO-O2.} + \text{CCO-O2.} = \#2 \text{ CO2} + \text{C-O2.} + \text{CCHO} + \text{RO2-R.} + \text{O2}$$

Notes

59	Assumed to have same rate constant as corresponding reaction of CH ₃ C(O)OO.
57	The products of the reactions of RCO-O ₂ . are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

Reactants, products and rate parameter are consistent with present knowledge. However it must be noted that acetaldehyde is formed only if there is sufficient NO_x to convert the produced CH₃CH₂O₂ to CH₃CHO.

Reaction PPPP

k(300)	A	Ea	Notes
Same as Reaction APAP			59,57

$$\text{RCO-O2.} + \text{RCO-O2.} = \#2 \{ \text{CCHO} + \text{RO2-R.} + \text{CO2} \}$$

Notes

59	Assumed to have same rate constant as corresponding reaction of CH ₃ C(O)OO.
57	The products of the reactions of RCO-O ₂ . are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.

Reactants, products and rate parameter are consistent with present knowledge. See comment about Reaction PPAP.

Reaction BPAP

k(300)	A	Ea	Notes
Same as Reaction APAP			62,63

$$\text{BZCO-O2.} + \text{CCO-O2.} = \#2 \text{ CO2} + \text{C-O2.} + \text{BZ-O.} + \text{R2O2.}$$

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO ₂ conversion, so it can be represented by BZ-O. + R ₂ O ₂ . The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

Reactants, products and rate parameter are consistent with present knowledge.

Reaction BPPP

k(300)	A	Ea	Notes
Same as Reaction APAP		62,57, 63	BZCO-O ₂ . + RCO-O ₂ . = #2 CO ₂ + CCHO + RO ₂ -R. + BZ-O. + R ₂ O ₂ .

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

Reactants, products and rate parameter are consistent with present knowledge.

Reaction BPBP

k(300)	A	Ea	Notes
Same as Reaction APAP		62,63	BZCO-O2. + BZCO-O2. = #2 {BZ-O. + R2O2. + CO2}

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

Reactants, products and rate parameter are consistent with present knowledge.

Reaction MPAP

k(300)	A	Ea	Notes
Same as Reaction APAP		62,64	MA-RCO ₃ . + CCO-O ₂ . = #2 CO ₂ + C-O ₂ . + HCHO + CCO-O ₂ . + O ₂

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO ₃ . And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO ₂ + CH ₂ =CH(.)CH ₃ , while the latter reacts with O ₂ to form HCHO + CH ₃ CO., as discussed by Carter and Atkinson (1996). The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

Reactants, products and rate parameter are consistent with present knowledge.

Reaction MPPP

k(300)	A	Ea	Notes
Same as Reaction APAP		62,64	MA-RCO ₃ . + RCO-O ₂ . = HCHO + CCO-O ₂ . + CCHO + RO ₂ -R. + #2 CO ₂

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO ₃ . And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO ₂ + CH ₂ =CH(.)CH ₃ , while the latter reacts with O ₂ to form HCHO + CH ₃ CO., as discussed by Carter and Atkinson (1996). The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

Reactants, products and rate parameter are consistent with present knowledge.

Reaction MPBP

k(300)	A	Ea	Notes
Same as Reaction APAP		62,64	MA-RCO ₃ . + BZCO-O ₂ . = HCHO + CCO-O ₂ . + BZ-O. + R ₂ O ₂ . + #2 CO ₂

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO ₃ . And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO ₂ + CH ₂ =CH(.)CH ₃ , while the latter reacts with O ₂ to form HCHO + CH ₃ CO., as discussed by Carter and Atkinson (1996). The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

Reactants, products and rate parameter are consistent with present knowledge.

Reaction MPMP

k(300)	A	Ea	Notes
Same as Reaction APAP		62,64	MA-RCO3. + MA-RCO3. = #2 {HCHO + CCO-O2. + CO2}

Notes

62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue.
64	MA-RCO3. And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher organic acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

Reactants, products and rate parameter are consistent with present knowledge.

Other Organic Radical Species**Reaction TBON**

k(300)	A	Ea	Notes
2.40e-11	2.40e-11	--	66,67 TBU-O. + NO2 = RNO3 + #-2 XC

Notes

66	The rate expression recommended by Atkinson (1997) for general alkoxy + NO2 reactions is $2.3 \times 10^{-11} \exp(+150/T)$. This is reduced by a factor of 1.58 to be consistent with environmental chamber data, as discussed in a separate note.
67	The effects of isobutane and t-butyl alcohol on ozone formation and radical levels in environmental chamber experiments are not consistent with predictions of models which assume the recommended rate constant ratios for the decomposition of t-butoxy radicals relative to reaction with NO2. The data are better fit if the ratio is increased by a factor of 2.5. The error is assumed to be equally distributed in each rate constant, so they are both adjusted by the a factor of 1.58, which is the square root of 2.5.

The reactants, products and rate parameter are consistent with the Atkinson (1997) recommendations. However the need to adjust the rate parameter to fit environmental chamber data raises concerns about the uncertainty of the rate parameter. Also since Atkinson (1997) recommends an Ea of -0.30 kcal mole⁻¹ it should be included in the rate parameter expression.

Reaction TBOD

k(300)	A	Ea	Notes	
1.18e+3	7.50e+14	16.20	68,67	TBU-O. = ACET + C-O2.

Notes

68	Atkinson (1997b) recommends the high-pressure rate expression of $6.0 \times 10^{14} \exp(-16.2/RT)$. Batt and Robinson (1987) calculate that at one atmosphere the rate constant is 79% the high pressure limit, giving an estimated rate expression of $4.74 \times 10^{-14} \exp(-16.2/RT)$. This is increased by a factor of 1.58 to be consistent with environmental chamber data, as discussed in a separate note.
67	The effects of isobutane and t-butyl alcohol on ozone formation and radical levels in environmental chamber experiments are not consistent with predictions of models which assume the recommended rate constant ratios for the decomposition of t-butoxy radicals relative to reaction with NO ₂ . The data are better fit if the ratio is increased by a factor of 2.5. The error is assumed to be equally distributed in each rate constant, so they are both adjusted by the a factor of 1.58, which is the square root of 2.5.

The reactants, products and rate parameter are consistent with present knowledge but the need to adjust the rate parameter to fit environmental chamber data raises concerns about the uncertainty of the rate parameter.

Reaction BRN2

k(300)	A	Ea	Notes
3.79e-11	2.30e-11	-0.30	69

**Notes**

69	The rate constant is based on the general recommendation of Atkinson (1994) for alkoxy + NO ₂ reactions at the high pressure limit. Nitrophenol formation has generally been assumed in this reaction (e.g., see Atkinson, 1990; Carter, 1990), presumably via some rearrangement of an initially-formed unstable adduct. However, based on lower than expected yields of nitrophenols in NO ₃ + cresol and OH + benzaldehyde systems (Atkinson, 1994), this may be an oversimplification.		
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The reactants and rate parameter are consistent with the Atkinson (1997) recommendations. The products are very uncertain.

Reaction BRH2

k(300)	A	Ea	Notes
Same k as rxn RRH2			70

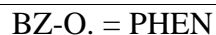
**Notes**

70	Assumed to have the same rate constant as the reaction of HO ₂ with peroxy radicals. This may underestimate the actual rate constant.		
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The rate parameter is highly uncertain but this approach is reasonable given the lack of measurements. It is not clear that the chosen rate parameter must be less than the actual rate parameter.

Reaction BRXX

k(300)	A	Ea	Notes
1.00e-3	1.00e-3	--	71

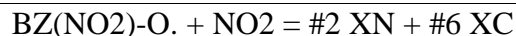
**Notes**

71	This is included to avoid problems if these radicals are ever formed under conditions where both HO ₂ and NO ₂ are very low (which is considered to be unlikely under most ambient conditions), and can be considered to represent its reaction with organics present. The rate constant is arbitrary, and is such that this process becomes significant only if [NO ₂] < ~3x10 ⁻⁶ ppm and [HO ₂] < 1x10 ⁻⁵ ppm.		
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This reaction is completely arbitrary and has been inserted to avoid potential numerical problems. It seems unlikely that the [NO₂] could become less than ~3E-6 ppm and [HO₂] become less than 1E-5 ppm while [BZ-O.] is significant.

Reaction BNN2

k(300)	A	Ea	Notes
Same k as rxn BRN2			72



Notes

72	The rate constant is based on the general recommendation of Atkinson (1994) for alkoxy + NO ₂ reactions at the high pressure limit. The products of this reaction (presumed to be aromatic dinitro compounds) are expected to have very low vapor pressures and are represented as unreactive nitrogen and carbon.
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The reactants and rate parameter are consistent with the Atkinson (1997) recommendations. The products are very uncertain and it could be that compounds more reactive dinitro aromatics are formed but given the lack of data this treatment is reasonable.

Reaction BNH2

k(300)	A	Ea	Notes
Same k as rxn RRH2		70	BZ(NO ₂)-O. + HO ₂ . = NPHE

Notes

70	Assumed to have the same rate constant as the reaction of HO ₂ with peroxy radicals. This may underestimate the actual rate constant.
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The rate parameter is highly uncertain but this approach is reasonable given the lack of measurements. It is not clear that the chosen rate parameter must be less than the actual rate parameter.